

Electrochemical behaviour of copper(II) at a hanging mercury drop electrode

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ABSTRACT: The electrochemical properties of Cu(II) ions were studied in 0.1 M KNO₃ at a hanging mercury drop electrode using cyclic and convolutive voltammetry in addition to chronoamperometry and chronopotentiometry methods. The Cu(II) ions consumed two electrons in two steps to form monovalent Cu(I) ions and Cu metal followed by a process of amalgam formation. The rates of both electron transfer steps were found to be quasi-reversible. Digital simulation was used to verify the electrode pathway and to determine and confirm the electrochemical parameters of the reductive process of bivalent Cu(II) ions.

KEYWORDS: convolutive voltammetry, electrode pathway, electrochemical parameters, Cu metal

INTRODUCTION

The use of copper compounds in medical application is well established¹. The immune system and thyroid gland health depend on copper level and any shortage in copper level may lead to the development of hyperthyroidism. In several biological reactions, copper is important as an electron donor. Copper deficiency is treated by taking cupric sulphate at doses up to 0.1 mg/kg daily. Some benefits of copper gluconate have been used in the treatment of osteoporosis, cardiac arrhythmia, wound healing, vascular disease, osteoarthritis, reducing high cholesterol levels in humans and rheumatoid arthritis.

After coordinating with metal ions, copper can play an important role in altering the pharmacological properties of known drugs². Drugs containing metal compounds such as antidiabetic, anti-inflammatory, antimicrobial, antimanic, antiulcer, and antiparasitic, antihypertensive agents have already been reported³. About 30–40% of all known proteins are metalloenzymes which need traces of metal cofactors such as Fe, Cu, Zn, Ni, Mn for their proper folding into an active 3D structure during biological processes^{4,5}.

In buffer solution of different pH, the volumetric measurements of Cu(II) in the presence of L-phenylalanine (Phe) and aspartic acid (Asp) has been carried out. The effect of scan rate and variation of Phe or Asp concentrations were demonstrated. In the presence of Phe and Asp, Cu(II) has been found

to undergo two cathodic peaks coupled with two-step two-electron transfer anodic reaction⁶.

Copper(II) salen undergoes a three-step reduction at a glassy carbon cathode, in dimethylformamide containing tetramethylammonium tetrafluoroborate; the first peak is due to the reduction of copper(II) to copper(I), the second one is due to the reduction of copper(I) to copper metal, and the third voltammetric peak arises from reduction of the dianion salen⁷. It is established that at low values of pH, Cu(II) was reduced electrochemically via two-step reduction mechanism, while at high pH it proceeds via one-step process⁸. Also, the electrochemical reduction of Cu(II) ion has been studied with various supporting electrolytes in acidic and basic media^{9,10}.

To the best of our knowledge, there is a shortage of studies dealing with the electrochemical behaviour of Cu(II) ions via convolutive voltammetry, chronoamperometry and chronopotentiometry. The present work therefore investigated the electrochemical behaviour of Cu(II) ions in aqueous KNO₃ solution as a supporting electrolyte. The electrochemical parameters were determined and the electrode pathway was suggested and verified using a digital simulation method.

MATERIALS AND METHODS

Chemicals

To prepare the solutions, we used CuSO₄ and KNO₃ reagents (analytical grade from Fluka). Triple dis-

tilled water was used as a solvent. The experiments were carried out in samples of Cu(II) at the concentration 2.5×10^{-4} M in 0.1 M KNO_3 as supporting electrolyte. The solutions were deaerated using nitrogen. The gas was passed over the solutions during the measurements.

Apparatus

A polarographic analyser (from EG & G) with a cell for cyclic voltammetry (CV) was used to conduct the experiments. The data of residual current were also stored and subtracted from the captured data set, minimizing the effects of double layer charging current. The measurements were performed with an electrode assembly Model 303A, with an HMDE (area = 2.61×10^{-2} cm²) as working electrode, Ag/AgCl as reference electrode, and a Pt wire as auxiliary electrode. CV experiments were investigated at scan rates in the range 0.02–5 V/s. Generation of the theoretical cyclic voltammograms was carried out by digital simulation using EG & G CONDESIM and finite difference techniques¹¹. For the simulation program, the algorithms were coded and executed into the package supplied by EG & G.

RESULTS AND DISCUSSION

Cyclic voltammetry measurements

The electrochemical behaviour of 2.5×10^{-4} M of the Cu(II) ions was studied in detail using cyclic voltammetry in 0.1 M aqueous solution of KNO_3 , at scan rates in the range of 0.02–5 V/s. Fig. 1 shows a typical response of Cu(II) at scan rate of 0.1 V/s after subtracting the background and correcting the

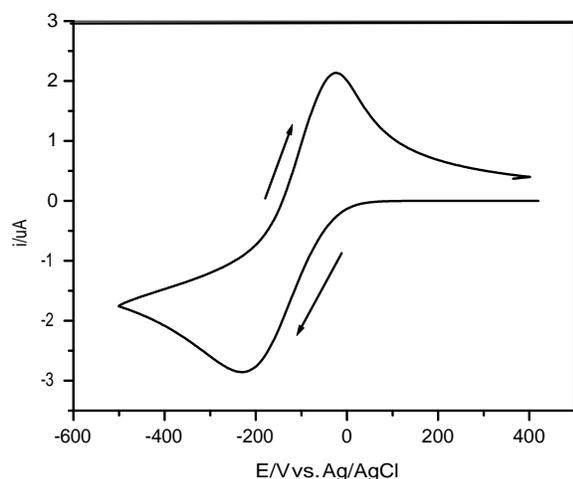


Fig. 1 Cyclic voltammogram of 2.5×10^{-4} M of Cu(II) in 0.1 M KNO_3 at a scan rate of 0.1 V/s.

Table 1 Values of wave characteristics of cyclic and deconvoluted voltammograms of Cu(II) ion at various scan rates.

Scan rate ν (V/s)	E_p (mV)	$E_p - E_{p/2}$ (mV)	ΔE_p (mV)	$W^{p/2}$ (mV)
0.1	230	124	212	187
0.2	251	136	240	211
0.5	289	143	273	234
1	342	163	303	251
2	366	187	337	278
5	462	201	354	292

uncompensated resistance. The cyclic voltammogram exhibits one broad cathodic peak coupled with one anodic peak.

It was found that the height of the cathodic and the anodic peaks increased as the scan rate increased, and the position of the cathodic and the anodic peaks depended on the scan rate. The variation in peak separation ($\Delta E_p = 113$ – 462 mV) in the studied range of the scan rate indicates that the rate of Cu(II) ion reduction proceeded moderately fast¹².

This means that the first step produces a univalent copper ion Cu(I) that accepts another electron to form copper metal which then combines with Hg to form copper amalgam. The ratio of the backward peak current to the forward one is less than unity, confirming the formation of copper amalgam¹³. It was found that the measured values of peak width, $E_p - E_{p/2}$, increased with the increasing scan speed (Table 1), confirming the quasi-reversibility of the rate of electron transfer. The variation of peak separation (ΔE_p) and the peak broaden with sweep rate was consistent with that of an overall two sequential moderate fast electron transfer reaction¹³.

The redox potential (E°) values of the two moderate fast charge transfer were determined from generated cyclic voltammograms. Accordingly, the electrode reaction might be suggested to proceed as two sequential quasi-reversible Faradaic processes followed by amalgam formation. The values of the first and second standard heterogeneous rate constants (k_1° and k_2°) of electron transfer were determined from the generated voltammograms and were found to be 1.40×10^{-5} m/s and 2.50×10^{-5} m/s, respectively¹⁴. In addition, the values of standard redox potentials (E_1° and E_2°) were 0.065 V and 0.115 V for the first and second electron transfer, respectively. The values of D_1 and D_2 were 5.40×10^{-9} m²/s and 5.85×10^{-9} m²/s,

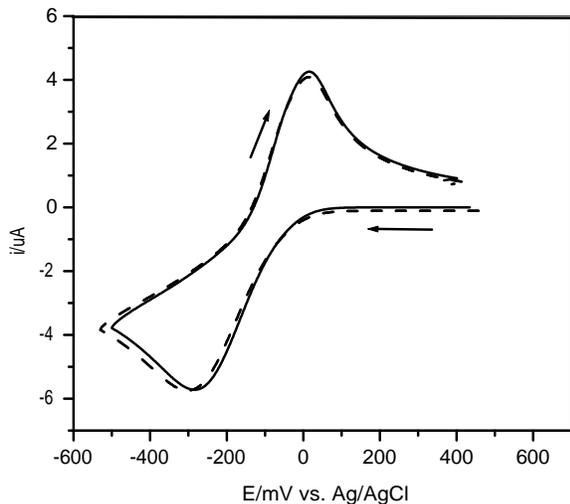


Fig. 2 Matching between experimental voltammogram of Cu(II) (solid line) and simulated voltammogram (dashed line) at a sweep rate of 0.2 V/s.

respectively; and the values of symmetry transfer coefficient α_1 and α_2 were 0.31 and 0.30, respectively.

It was found that the plot of i_p versus \sqrt{v} produced a nonlinear curve, indicating that the reaction deviates from the behaviour of two one-step electron transfers. This behaviour confirmed the presence of two sequential electron transfer steps. Fig. 2 shows the experimental and theoretical calculations of the electrochemical parameters for Cu(II) ions; clearly the results demonstrate good agreement between the captured data and the simulated data.

The mechanism proposed here was confirmed and verified by generating the following simulated cyclic voltammograms: (i) $E_{n=1}E_{n=1}$ scheme using the values of calculated electrochemical parameters at different values of separation between the first and the second redox potentials ($\Delta E'^{\circ}$). The values selected for $\Delta E'^{\circ}$ are 100 mV, 150 mV, 200 mV, 250 mV, 300 mV, and 350 mV (Fig. 3), and (ii) $E_{n=2}$ scheme, where n is the number of electron transfer and the symbol E refers to the electron transfer.

In the case of the EE scheme, when $\Delta E'^{\circ} \geq 100$ mV, there is a disagreement between the experimental voltammograms and the theoretical voltammograms which confirms the proposed mechanism. In addition, in the case of simple electron transfer ($E_{n=2}$ scheme), there is a large deviation between the experimental voltammogram of bivalent Cu(II) and the generated cyclic voltammogram of $E_{n=2}$

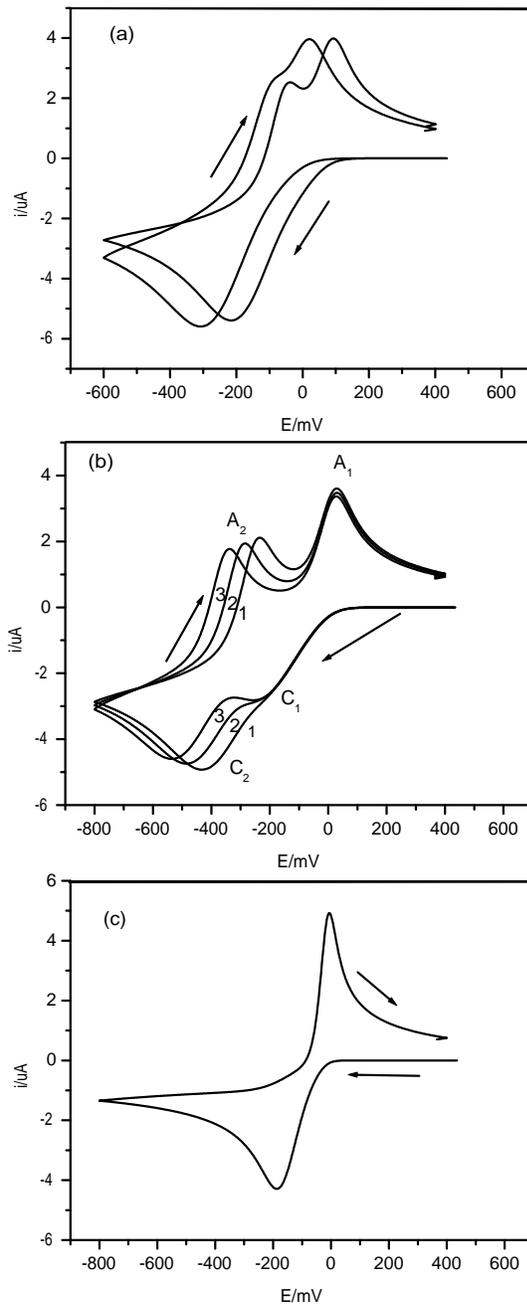


Fig. 3 Simulated cyclic voltammograms of EE scheme when (a) $\Delta E'^{\circ} = 100$ mV and 150 mV; (b) $\Delta E'^{\circ} = 250$ mV, 300 mV, and 350 mV, labelled 1, 2, and 3, respectively; and (c) $\Delta E'^{\circ} = 0.0$.

scheme (Fig. 3).

In the case of sequential two-charge transfer processes, there are two activation barriers. The free energy of the activated complex of the first step (ΔG^{\ddagger}) can be calculated from the standard

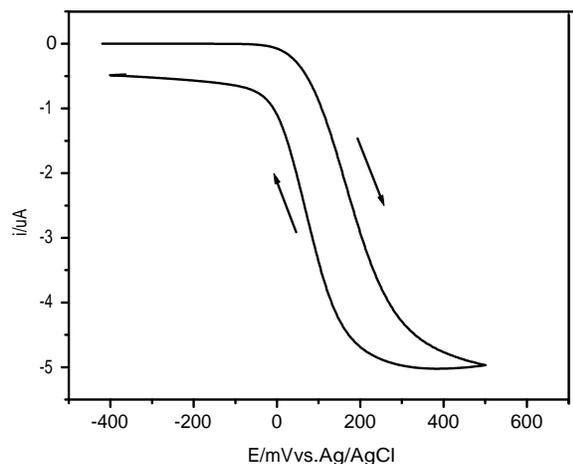


Fig. 4 Convolution voltammery (I_1) of the reductive process of Cu(II) ion sweep rate of 0.2 V/s.

heterogeneous electron transfer using the following equation^{15,16}:

$$\Delta G_{\text{exp}}^{\#} = 0.05915(4 - \log k^{\circ}) \text{ eV at 298 K.}$$

It was found that the value of $\Delta G^{\#}$ was 9.08 J/mol for the first electron transfer.

Convolution transforms

The following equation defines I_1 convolution^{17,18}:

$$I_1(t) = \frac{1}{\sqrt{\pi}} \int_0^t \frac{i(u)}{\sqrt{t-u}} du.$$

It is used for the electroactive species diffusion coefficient determination using¹⁷:

$$I_{\text{lim}} = (n_1 + n_2)FAC\sqrt{D}, \tag{1}$$

where I_{lim} is the limiting convoluted current of I_1 , n_1 and n_2 are the number of electrons transferred, F is the Faraday constant (96 500 C/mol), A is the electrode surface area, C is the bulk concentration of electroactive species, and D is the diffusion coefficient (m^2/s). The calculated value of the diffusion coefficient (D) via (1) is equal to $5.1 \times 10^{-9} \text{ m}^2/\text{s}$. The I_1 convolution of Cu(II) at 0.2 V/s scan rate is shown in Fig. 4.

The curve in Fig. 4 exhibits a separation between the forward and the reverse sweep of the I_1 convolution, and the reverse sweep of I_1 convolution does not return to zero, which might be attributed to amalgam formation and confirming two sequential electron transfer mechanism with moderate speed of the rate of two electron transfer

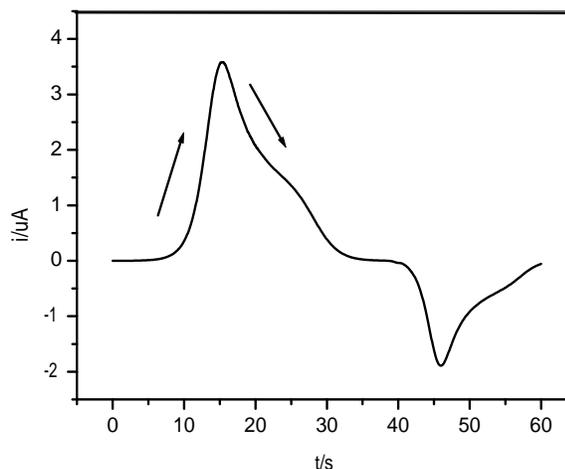


Fig. 5 Plot of i versus t corresponding to a reductive cyclic voltammogram at the sweep rate of 0.2 V/s. The point $t = 25.4 \text{ s}$ is the time at which the potential scan is switched to the reverse direction.

between the HMDE and Cu(II) ion, i.e., moderately fast EE mechanism followed by amalgam formation.

For an electron transfer in the case of a quasi-reversible reaction, the equation is adapted¹⁹ to:

$$E = E^{\circ} + \frac{RT}{\alpha nF} \ln \left(\frac{k^{\circ}}{i\sqrt{D}} (I_{\text{lim}} - I(1 + e^{(nF/RT)(E-E^{\circ})})) \right).$$

Thus in the case of simple electron transfer (E scheme) the presentation of

$$\ln \left(\frac{1}{i} (I_{\text{lim}} - I(1 + e^{(nF/RT)(E-E^{\circ})})) \right) \text{ versus } E$$

gives a straight line with the slope of $\alpha nF/RT$. Hence a nonlinearity of the plot confirms the presence of two quasi-reversible electron transfer (EE) mechanism with close values of two redox potential in the investigated system.

Fig. 5 shows the plot of i versus t of the voltammogram at the scan speed of 0.2 V/s. The exhibited discontinuity Δi_c at $t = 25.4 \text{ s}$ is due to the reversibility of the scan. The Cottrell plot is presented as i versus $1/\sqrt{t}$. The slope of the i versus $1/\sqrt{t}$ plot yields a diffusion coefficient $D = 5.4 \times 10^{-9} \text{ m}^2/\text{s}$. Clearly from Fig. 5 the height ratio of the forward peak to the reverse peak is different from the one confirming the existence of amalgam formation¹³.

Deconvolution transforms

The deconvolution transforms (dI_1/dt) as a function of E of reversible electrode process is defined

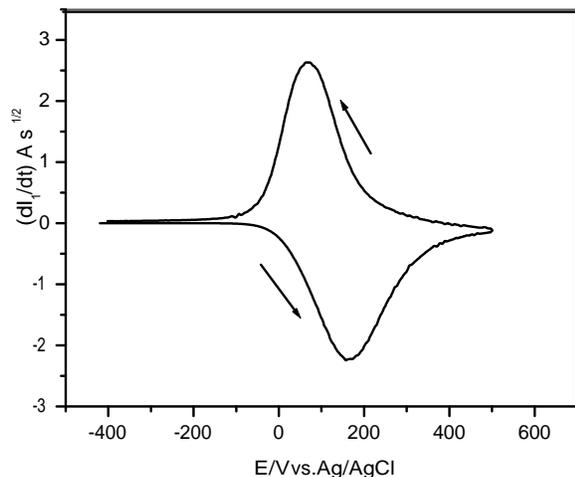


Fig. 6 Deconvolution voltammetry (dI_1/dt) of the reductive cyclic voltammogram of Cu(II) at a sweep rate of 0.2 V/s.

as¹²:

$$e_p = \frac{d^{1/2}i}{dt^{1/2}} = \frac{dI_1}{dt} = (n_1 + n_2)FAC\sqrt{D}a \frac{\zeta}{(1 + \zeta)^2}, \quad (2)$$

in which the parameters a and ζ are defined as

$$a = \frac{nvF}{RT},$$

$$\zeta = \exp\left(\frac{nF}{RT}(E - E^*)\right).$$

The image of dI_1/dt produces two peaks with a maximum and minimum amplitude alignment at $E_{1/2}$ values in the case of rapid electron transfer and $T = 298$ K. A plot of (2) using $v = 0.2$ V/s in 0.1 M KNO_3 is shown in Fig. 6. The peak width of deconvolution $W^{p/2}$ in the case of fast electron transfer is equal to $3.53RT/nF = 90.5/n$ mV. In this communication, the measured $W^{p/2} = 211 \pm 2$ mV, confirming the quasi-reversibility of the charge transfer.

Moreover, the asymmetry and the deviation from the alignment point of the forward and the backward sweep confirm the quasi-rapidity of both charge transfer of the electroreduction Cu(II) ions process. The peak height was also proportional to Cu(II) concentration, to the area of electrode surface, to the number of electrons, and to the scan speed v . It was found that the convolutive and deconvolutive voltammetry curves were much easier to understand and to interpret than the cyclic voltammetry curves.

In addition, the diffusion coefficient (D) values

were calculated using the following relationship¹³:

$$I_{\text{lim,d}} = \frac{i_p}{3.099\sqrt{an_a v}},$$

where $I_{\text{lim,d}}$ is the limiting convoluted current deduced from CV and I_1 , i_p is the peak current of the quasi-reversible electrode reaction, n_a is the number of electrons participating in the rate determining step, and v is the scan rate. The values of D calculated from $I_{\text{lim,d}}$ agree well with those calculated from the convolution voltammetry and the digital simulation.

In addition, a simple and accurate method to calculate the number of electrons consumed in the electrode reaction¹³ is

$$n = \frac{0.086 e_p}{I_{\text{lim}} \alpha v},$$

where e_p is the height of deconvoluted peak current and the other symbols have their usual meaning. The calculated number of electrons ($n = n_1 + n_2$) was found to be 2.05 for the overall reduction process.

In this work, the first-order derivative voltammetry (e^-) is presented. This method exhibits high sensitivity, resolution, reproducibility, and rapidity of the system. The presentation of e^- versus E calculated by G1 algorithms for electroreduction of Cu(II) ion at the scan speed of 0.2 V/s indicates that the height of the forward peak increases with an increase in the scan rate and the position of peak potential shifted to more cathodic potential. This behaviour agrees well with cyclic voltammetry and deconvoluted voltammetry, and indicates that the quasi-reversible nature of the two electron transfer involved in the electroreduction of bivalent Cu(II) ion closely with two redox potentials.

From this study, it can be concluded that the redox potential for the first reduction process is slightly less negative than the second one, which shows that the first process requires less energy than the second one.

Chronoamperometric study

Stepping the potential from an initial potential (E_i) to a final one (E_f), and recording the current as a function of time are the basis of chronoamperometry experiment. Chronoamperogram of 2.5×10^{-4} M solution of the Cu(II) ion in 0.1 M KNO_3 at HMDE, with $E_i = -0.05$ V and $E_f = -0.25$ V, is shown in Fig. 7. The forward rate constant k_f was determined via the following equation¹⁴:

$$i(t) = -\beta I_1 + u,$$

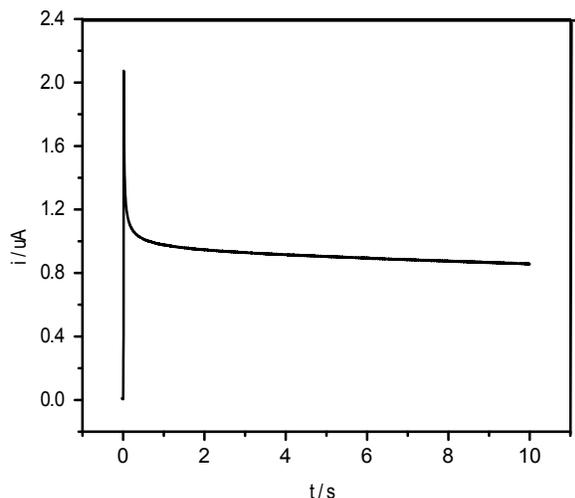


Fig. 7 Chronoamperogram of 2.5×10^{-4} M of bivalent Cu(II) ion in 0.1 M KNO_3 .

where $u = (n_1 + n_2)FACk_f\sqrt{D}$ and $\beta = k_f\sqrt{D}$. The slope of the linear plot of $i(t)$ versus I_1 and the intercept at $I_1 = 0$ produce the value of k_f .

Here the correlation between the rate constant (k_f), the electrode potential (E), and the electron transfer is investigated by the Butler-Volmer treatment using the equation¹⁴:

$$\log k_f = \frac{\alpha n F}{RT} (E_f - E'^{\circ}) + \log k^{\circ} \quad (3)$$

The slope of the linear plot for $\log k_f$ versus $E_f - E'^{\circ}$ gives an α value of 0.34. The standard heterogeneous rate constant k° value was found to be 2.65×10^{-5} m/s from the point at which $E_f = E^{\circ}$. Both values agreed well with those calculated from the digital simulation and the cyclic voltammetric data.

Chronopotentiometric investigation

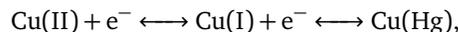
Solution of 2.5×10^{-4} M of Cu(II) in 0.1 M KNO_3 at HMDE displayed chronopotentiogram with only one reduction transition time in agreement with the result obtained from cyclic voltammetry. The following equation was used to analyse the chronopotentiometric transition time¹⁸:

$$I_{\text{lim}} = 2i_c \sqrt{\frac{t_s}{\pi}} = (n_1 + n_2)FAC\sqrt{D}, \quad (4)$$

where i_c is the polarization current, t_s is the transition time of the bivalent Cu(II), and the remaining terms have their usual meaning. The value of the diffusion coefficient D calculated from chronopotentiometry compares well with that obtained from

each of I_1 convolution, deconvolution voltammetry, and digital simulation methods.

According to the above discussion, the reductive electrode behaviour of bivalent Cu(II) ion can be suggested to proceed as



i.e., EE mechanism with copper amalgam formation process.

CONCLUSIONS

In this article, the electrochemical behaviour of bivalent Cu(II) ion was investigated at HMDE in 0.1 M KNO_3 using cyclic voltammetry combined with convolutive voltammetry, chronoamperometry, and chronopotentiometry techniques. The results of this study summarize the reports of electrochemical studies of Cu(II) ion and show that the electrode process of Cu(II) ion in 0.1 M KNO_3 at a mercury electrode proceeds as two consecutive electron transfer and produces one broad reductive peak coupled with one broad anodic peak. This behaviour indicates that the first charge transfer produces a univalent Cu(I) ion that accepts another electron to give Cu metal which combines with mercury to form Cu(Hg). The kinetic parameters calculated experimentally were confirmed using a digital simulation method.

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